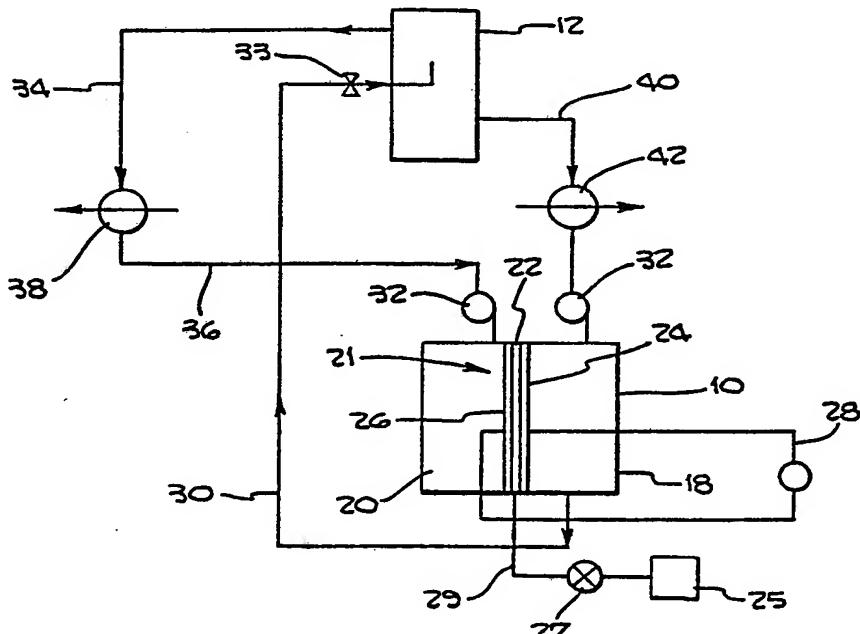




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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## (54) Title: GAS-PERMEABLE AND ION-PERMEABLE MEMBRANE FOR ELECTROCHEMICAL SYSTEM



## (57) Abstract

An electrode apparatus adapted for use in electrochemical systems (10) having an anode compartment (20) and a cathode compartment (18) in which gas and ions are produced and consumed in the compartments during generation of electrical current. The electrode apparatus includes a membrane (22) for separating the anode compartment from the cathode compartment wherein the membrane (22) is permeable to both ions and gas. The cathode (24) and anode (26) for the assembly are provided on opposite sides of the membrane (22). During use of the membrane-electrode apparatus in electrochemical cells, the gas and ions generated at the cathode (24) or anode (26) migrate through the membrane (22) to provide efficient transfer of gas and ions between the anode compartment (20) and cathode compartment (18).

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-1-

1                   Gas-permeable and ion-permeable membrane for  
electrochemical system.

5                   This invention was made with United States Government  
support under Contract No. EG-77-C-01-4042 awarded by the  
Department of Energy. The U.S. Government has certain  
rights in this invention.

BACKGROUND OF THE INVENTION

10

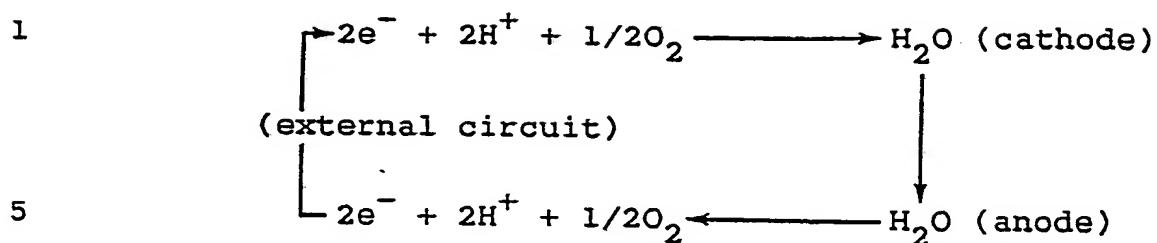
1. Field of the Invention

15                   The present invention relates generally to batteries  
and systems which convert chemical energy into electrical  
energy by use of a continuous concentration  
electrochemical cell. More specifically, the present  
invention relates to an improved gas-permeable electrode  
for use in such systems.

20                   2. Description of the Background Art

25                   U.S. Patent No. 3,231,426, issued January 25, 1966,  
discloses a continuous concentration cell in which a  
voltage is obtained and an electric current is generated  
between a cathode immersed in concentrated sulfuric acid  
and an anode immersed in dilute sulfuric acid. The  
reaction cycle which is set up between the electrodes is:

2



During operation of the cell, the concentrated sulfuric acid solution is diluted by water generated at the cathode, while the dilute sulfuric acid solution becomes more concentrated due to the generation of acid at the anode. The difference in acid concentration between the two solutions must be maintained in order to provide continuous generation of electrical energy. The system disclosed in U.S. Patent No. 3,231,426 maintains the acid concentration gradient by heating the concentrated acid solution to distill off water generated at the cathode. The water which is continuously distilled from the concentrated acid solution is cycled to the dilute acid solution to continually provide dilution of the acid which is generated at the anode. Continuous concentration cells of the type described above utilize porous electronically non-conducting beds or barriers between the electrodes which typically are made from felted asbestos fibers, glass fibers or ceramic compositions such as alumina, zirconium oxide, ion exchange membranes, or porous organics, such as polypropylene or cellulose.

Another type of thermoelectrochemical system has been developed which functions as a low-temperature power converter in which the electrochemical cell reactants are thermally regenerated at a temperature below about 250°C.

This type of thermoelectrochemical system basically includes an electrochemical cell having a cathode compartment and an anode compartment. The two compartments have a common ion permeable separation wall.

1 which allows ions to pass between the two compartments but  
prevents the passage of gas. A hydrogen ion reacting  
cathode and a hydrogen ion reacting anode are located  
within their respective compartments with the cathode and  
5 anode being connectable externally from the system for  
generation of an electrical voltage and current between  
the electrodes.

10 A cathode fluid comprising a chosen Bronsted acid is  
typically located in the cathode compartment and in  
contact with the cathode. During one method of operation  
of the system, hydrogen gas is generated or collected at  
the cathode and the acid is consumed. The system further  
includes an anode fluid comprising a chosen Bronsted base  
15 which is located in the anode compartment and in contact  
with the anode. During one method of operation of the  
system, a cation of the base is generated and the base and  
hydrogen gas are consumed at the anode. At least one of  
the components, i.e., acid or base, comprises an organic  
material.

20 Because of the gas-impermeability of the ion-permeable  
separation wall, any hydrogen gas generated at the cathode  
during operation of the system is transferred externally  
to the anode compartment for consumption at the anode  
during generation of the electrical current. In addition,  
25 during operation of the system, the anions of the acid  
and/or the cations of the base migrate through the ion  
permeable separation wall into the anode or cathode  
compartment, respectively, where they combine with the  
cation of the base or the anion of the acid to form the  
30 corresponding salt. A feature of this system is that the  
salt is capable of being thermally decomposed at a  
temperature below about 250°C to directly form the acid  
and base as two decomposition products. These products  
can be separated to regenerate the acid and base.

1        A thermal regenerator is provided in these systems for  
thermally converting the salt directly to the acid and  
base starting materials, at a temperature below about  
250°C. Means for transferring the salt from the anode  
5        and/or cathode compartment to the thermal regenerator are  
also provided. Anode recycle means are provided for  
transferring the base formed in the thermal regenerator  
back to the anode compartment to replenish the base  
consumed during operation of the system. Cathode recycle  
10      means are also provided for transferring the acid formed  
in the thermal regenerator back to the cathode compartment  
to replenish the acid consumed during operation of the  
system.

15      The above-described systems are particularly useful  
because their relatively low operating temperatures (i.e.  
below 250°C) allow them to be used in recovering waste  
heat in the form of electric power from internal  
combustion engines, industrial processes, and the like.  
They can also be used to convert heat from other sources  
20      such as solar energy, fossil or nuclear fuel, oil well  
heads or other geothermal heat sources.

25      An important consideration in thermoelectrochemical  
systems, as well as electrochemical systems, in general,  
is the overall efficiency of the system and the useful  
life. It is therefore desirable to continually search for  
improvements to such systems in which the performance,  
efficiency and life of the system are maximized.

#### SUMMARY OF THE INVENTION

30

35      In accordance with the present invention, a means is  
provided for improving the performance, reliability, and  
efficiency of electrochemical systems by reducing the  
complexity and internal electrical resistance of such  
systems.

The present invention involves the discovery that suitable separation walls between the cathode and anode compartments can be made which are permeable to both ions and gas. The provision of a gas-permeable and 5 ion-permeable separation wall or membrane eliminates the need for externally transferring gases between the two compartments. This elimination of external gas transfer in accordance with the present invention reduces the internal resistance of the system and increases the 10 efficiency of electrical and gas transfer between the anode and cathode compartments.

The present invention is based on an electrode apparatus which is adapted for use in electrochemical systems having anode and cathode compartments wherein the 15 apparatus includes an anode and cathode between which is located a membrane having a cathode side and an anode side and wherein the membrane includes both ion-permeable and gas-permeable regions to provide transfer of ions and gas between the cathode and anode.

20 The electrode apparatus of the present invention has application to any electrochemical system in which gas must be passed between the anode and cathode and may be used in place of existing membrane barriers or other barriers designed to provide selective passage of ions 25 between anodes and cathodes. The invention is especially well suited for use in the continuous concentration systems or acid/base systems described above.

The electrode apparatus of the present invention is 30 based upon the use of an ion-permeable and gas-permeable membrane as the separator wall or barrier between the anode and cathode compartments of an electrochemical cell. It is preferred that the cathode and anode be placed as close to the membrane separator wall as possible 35 in order to reduce the internal resistance of the cell due to ion migration through the electrolyte solutions and to

1 reduce the distance that gas must move from its reaction  
site to or from the gas passage pores in the membrane. As  
a particular feature of the present invention, the anode  
and cathode are provided as porous coatings or thin layers  
5 contacting opposite sides of a gas- and ion-permeable  
membrane. This reduces the internal resistance of the  
cell because the ions and gas generated at the electrodes  
do not have to travel through any extensive distance in  
the liquid phase to reach the opposite electrode.

10 These and many other features and attendant advantages  
of the present invention will become apparent as the  
invention becomes better understood by reference to the  
following detailed description when considered in  
conjunction with the accompanying drawings.

15

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 FIG. 1 is a schematic representation of an exemplary  
thermoelectrochemical system utilizing the present  
invention.

FIG. 2 is a cross-sectional representation of a  
preferred electrode apparatus in accordance with the  
present invention.

25 FIG. 3 is a cross-sectional representation of an  
alternate preferred electrode apparatus in accordance with  
the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

30 An exemplary system in which the gas-permeable and  
ion-permeable membrane of the present invention can be  
used is shown in FIG. 1. The system basically includes an  
electrochemical cell 10 and a thermal regenerator 12.  
However, it is to be understood that the present invention  
35 is not limited to a thermoelectrochemical system, but may

1 be used in any electrochemical system as generally indicated at 10 in FIG. 1.

5 The electrochemical cell 10 includes a cathode compartment 18 and an anode compartment 20. The cathode and anode compartments 18 and 20 are separated by a preferred exemplary electrode apparatus as shown generally at 21. The electrode apparatus 21 includes a central membrane 22 which is permeable to both gas and ions. The membrane 22 is located between and in contact with an 10 anode 26 and a cathode 24.

15 The requirements for membrane 22 are that it must be a permeable membrane or barrier which allows cation and/or anion exchange (i.e., a cation-exchange membrane, an anion-exchange membrane or a microporous membrane for cation and anion exchange), while at the same time allowing gas transfer. The choice of the ion selectivity of the membrane depends on the particular electrochemical cell reaction of interest. In accordance with the present invention, gas- and ion-permeable regions coexist in the 20 membrane. The permeability of these regions depends on the diameter of the "pores" in these regions and the degree of hydrophobicity of the walls of the pores. In addition, the cell liquids in the anode and cathode compartments must have sufficiently high surface tensions 25 so that the hydrophobic material is not wetted by the liquids. Organic systems containing enough water or other high surface tension solvent to give surface tensions in excess of about 35 dynes per centimeter have been found to be suitable. Thus, in accordance with the present 30 invention, high surface tension liquids are excluded from the small pores of the membrane. Consequently, liquid ionic solutions will not pass through the small pores, whereas gas is able to pass through the small pores. As the pore size is increased, the hydrophobicity of the 35 walls exerts less effect, and the liquid ionic solutions

1 can pass through the larger pores. While it is  
advantageous to have both hydrophobic and hydrophilic  
regions in close proximity in the membrane, a purely  
hydrophobic material can be used if it has a sufficient  
5 distribution or dispersion in the diameters of its pores.  
A large hydrophobic pore will not exclude liquid, whereas  
a small hydrophobic pore will exclude liquid.

10 Suitable membranes or barriers which provide the  
desired ion- and gas-permeability can be made in a number  
of different ways. For example, a mesh, cloth, paper,  
porous film or felt of gas-permeable hydrophobic materials  
having openings or pores of varying size can be used to  
provide a barrier wherein gas is transported through the  
smaller diameter pores or passages in the fiber mesh,  
15 cloth, paper, felt or porous film and the ions are allowed  
to pass through the larger openings in the mesh, cloth,  
paper, felt, or porous film. Suitable materials for  
forming such a mesh, cloth, paper, porous film, or felt  
include non-conducting carbon fiber, expanded teflon, or  
20 porous polypropylene. (Teflon is a polytetrafluoro-  
ethylene manufactured by E.I. DuPont de Nemours of  
Wilmington, Delaware.) The term "porous teflon" as used  
herein is intended to include "expanded teflon," as is  
known in the art. The selected material should have a  
25 fine porosity, with sizes below 10 micrometers being  
preferred. For example, when using expanded teflon, the  
preferred pore size is within the range of about 1 to 3  
micrometers. For Celgard 2400 and 2500, preferred pore  
sizes are about 0.02 and 0.4 micrometers, respectively.  
30 The actual fiber size and the size of the openings through  
the mesh can be varied depending upon the particular  
electrochemical cell, to provide desired rates of gas or  
ion transfer.

35 Alternatively, suitable membranes can be formed from a  
felt, mesh, cloth, paper or porous film of gas-permeable

1      fibers or matrices, impregnated with an ion-exchange  
membrane material. Examples of the latter are specified  
below. Suitable matrices or fibers include electronically  
non-conducting carbon fiber, and expanded teflon or porous  
5      polypropylene matrices. In such a membrane, the gas  
passes through the fiber or matrix while the ions pass  
through the ion-exchange regions.

10     Suitable membranes can also be made by treating  
gas-permeable membranes so as to provide regions within  
these otherwise ion-impermeable membranes through which  
ions can be transported. For example, hydrophobic  
15     polypropylene, such as that marketed by Celanese Corp.  
(Charlotte, North Carolina) as Celgard 2500, can be  
treated with drops of a solution of a cation or anion  
exchange membrane material which, when cured, provides  
ion-permeable regions at selected spaced locations in the  
otherwise ion-impermeable material. Solutions of such ion  
exchange membrane materials are available commercially,  
20     for example, from Solution Technology, Inc. of Mendenhall,  
Pennsylvania. An exemplary material is Nafion. Nafion is  
a trademark of E.I. DuPont de Nemours of Wilmington,  
Delaware, for a polymer of polytetrafluoroethylene with  
fluorinated ether side chains terminated with sulfonic  
acid groups. Another exemplary material is an  
25     alkali-resistant copolymer of vinyl chloride and  
acrylonitrile with quaternary nitrogen groups, available  
from Ionics, Inc. of Watertown, Massachusetts. The  
preferred procedures for preparing the gas- and ion-  
permeable membranes are discussed in detail below. In  
30     addition to polypropylene, other membrane materials can be  
used such as microporous polytetrafluoroethylene (PTFE).

35     Other suitable membranes for practicing the present  
invention can be made by treating hydrophobic membranes  
with hydrophilic surfactants so as to provide ion-  
permeable regions within these otherwise gas-permeable

1 (ion-impermeable) membranes. For example, hydrophobic  
polypropylene, such as that marketed by Celanese Corp.  
(Charlotte, North Carolina) as Celgard 2400, can also be  
made hydrophilic by treatment with a surfactant, and this  
5 product is sold as Celgard 3400. By surfactant treatment  
at selected spaced locations in the otherwise ion-  
impermeable material, both liquid and gas can be  
transported through the modified membrane.

10 As yet another alternative, suitable membranes for  
practicing the present invention may be made by providing  
openings or holes in an ion exchange membrane such that  
gas but not ions can pass through the holes. The size and  
distribution of the holes can be determined for each  
15 particular electrochemical system used. Optionally, the  
membrane may be provided as a porous woven material, such  
as porous woven Nafion, obtained from E.I. DuPont of  
Wilmington, Delaware, and the gas passes through the  
openings in the woven material.

20 The membrane 22 is preferably as thin as possible  
without jeopardizing the structural integrity of the  
membrane. Membrane thicknesses on the order of about 1 to  
10 mils (0.025 to 0.25 mm) have been found satisfactory  
and thicknesses of less than 5 mils (0.125 mm) are  
desirable.

25 The relative size of the areas of gas permeability and  
ion permeability in the membrane along with respective  
permeabilities can be varied to suit the particular  
electrochemical cell and the required ion and gas  
transport. The degree of either gas or ion transport must  
30 be sufficient to avoid large current-resistance (IR) drops  
through the membrane or significant concentration  
polarization in either the anode or cathode compartment.

35 Both the cathode 24 and the anode 26 are hydrogen  
electrodes (i.e., electrodes which react with hydrogen gas  
or hydrogen ions) and are porous to allow the passage of

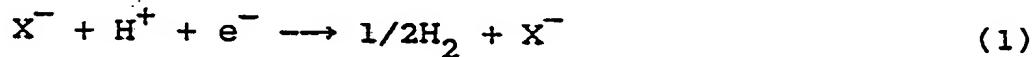
1       gas and ions through the electrode. One type of hydrogen  
electrode comprises a platinized porous carbon - teflon  
fuel cell electrode and is known in the art and  
commercially available. Another type of hydrogen  
5       electrode comprises a fine-mesh screen of tantalum,  
stainless steel, or other non-corrosive metal covered with  
platinum black. Still another type of hydrogen electrode  
is referred to as a solid polymer electrolyte (SPE)  
electrode and comprises a structure in which  
10      electrocatalyst is bonded directly to both sides of a  
solid polymer ionomer membrane to form the cathode and  
anode. In one method of construction of an SPE electrode,  
the catalyst in the form of a fine powder is mixed with  
teflon emulsion solution and sintered at about 345°C.  
15      The sintered teflon-bonded catalyst is then bonded to the  
SPE membrane at elevated temperature and under pressure.  
Another SPE electrode construction comprises the sintering  
of a porous electrode using material made from carbon or  
graphite powder and PTFE mixed with a platinum catalyst or  
20      PTFE alone mixed with a platinum catalyst. This porous  
electrode material is preferably placed in direct contact  
with the membrane so that the membrane 22 is sandwiched  
between the two electrodes 24 and 26. This electrode  
material can also be bonded to both sides of the membrane  
25      with heat and pressure and/or glued to the membrane using  
ion exchange solutions, such as from Solution Technology,  
Inc., or prepared by known processes, such as described by  
Moore and Martin in Analytical Chemistry, Vol. 58, 1986,  
pages 2569-2570. In accordance with the present  
30      invention, the porosity of the electrode material must be  
sufficient to allow transport of ions and gas while still  
providing the desired cathode or anode functions. Since  
the electrode is depolarized both from the back (solution  
side) and from the front (membrane side), the electrode

I must be thin enough so this dual polarization can be kept to a minimum. A thickness of less than 20 mils (0.5 mm) is desirable.

5 The hydrogen gas necessary for operation of the hydrogen electrode is introduced into the electrode apparatus 21 from hydrogen reservoir 25 by way of control valve 27 and transfer line 29. Generally, once the membrane 22 is saturated with gas, no additional gas need be supplied except that which is needed to replace gas 10 which escapes from the structure. This amount is quite small and can be made up by separating escaped gas from the liquid streams. In an optimized system this amount should be zero.

15 Referring again to the overall system of FIG. 1, the cathode compartment 18 includes a cathode fluid which is in contact with cathode 24. In a preferred thermoelectrochemical system, the cathode fluid is typically a Bronsted acid, i.e., a proton donor. The acid is chosen so that the anion of the acid combines with the 20 cation of the base to form a salt which can be thermally decomposed at a temperature below about 250°C to directly form the acid and base as two decomposition products which can be separated to regenerate the acid and base starting materials for the electrochemical cell 25 reaction.

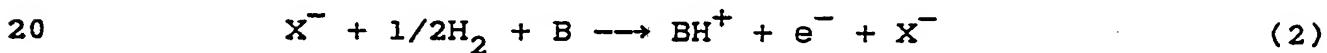
30 The cell reaction of the acid at the cathode 24 is shown in Equation (1) below, where hydrogen gas is generated or collected and acid is consumed at the cathode. The anion of the acid may have a valence other than that indicated in Equation (1).



where  $X^-$  = anion of acid

1       Acids which are used in this particular system include  
inorganic acids such as concentrated hydrochloric acid or  
phosphoric acid and organic acids such as methylsulfonic  
acid, trifluoromethylsulfonic acid, acetic acid, benzoic  
5       acid, and the borate ester formed by condensation of boric  
acid with ethylene glycol. A solvent may optionally be  
used with the acid.

An anode fluid is located in the anode compartment 20 for contact with anode 26. The anode fluid for a preferred thermoelectrochemical system is typically a Bronsted base, i.e., a proton acceptor. The base is chosen so that the cation of the base combines with the anion of the acid to form a salt which can be thermally decomposed at a temperature below about 250°C to form two separable decomposition products and regenerate the acid and base, as previously discussed. The cell reaction of the base at a hydrogen anode is shown in Equation (2) below.



where  $X^-$  = anion of acid

B = base

25 Thus, during the cell reaction, a cation of the base  
is generated and hydrogen is consumed at the anode. Bases  
which may be used in this particular system include  
inorganic bases such as ammonia or phosphine, and organic  
bases such as pyridine, aniline, triethanolamine,  
monoethanolamine, or diethylamine. A solvent may  
30 optionally be used with the base. Typically, either the  
acid or the base or both comprise an organic material.

As shown in FIG. 1, the electrodes 24 and 26 are connected to an external circuit schematically shown as 28 for generating an electrical current and voltage. The external circuit 28 can include electric motors or other

I systems for utilizing the electric energy generated by cell 10, or batteries or other suitable systems for storing the electric energy generated by cell 10.

In order to continually regenerate the acid and base consumed during operation of cell 10, the salt formed by the combination of the cation of the base and the anion of the acid is thermally decomposed. To accomplish this decomposition and regeneration, the electrolyte containing the salt is removed from the cell 10 and transferred to the thermal regenerator 12. If the salt is formed in the anode compartment 20, the anode solution is transferred to the thermal regenerator 12. If the salt is formed in the cathode compartment 18, the cathode solution is transferred to the thermal regenerator 12. If the salt is formed in both the anode and cathode compartments (20, 18), both the cathode and anode solutions are transferred to the thermal regenerator 12. For the sake of simplicity, FIG. 1 shows only one alternative, that in which the salt is formed in the cathode compartment 18, but the apparatus may be readily modified to accommodate the other alternatives mentioned.

In FIG. 1, the cathode solution is continually removed from the cell via line 30 and transferred to the thermal regenerator 12 utilizing pump 32 or other liquid transfer device. The cathode solution transferred in line 30 contains the salt in a solvent in the same concentration as present in the cathode compartment 20. In the thermal regenerator 12, the transferred cathode solution is heated to a temperature below about 250°C to thermally decompose the salt  $BH^+X^-$  to form the acid and base, as shown in Equation (3) below.



where B = base

35  $X^-$  = anion of acid

1        The acid and base must be capable of being separated. If either the acid or base is volatile and the other is not, then the volatile component may be condensed and returned to the cathode compartment 18 if it is the acid 5 or the anode compartment 20 if it is the base.

As shown in FIG. 1, the volatile base flows out of thermal regenerator 12 into line 34 where it is cooled and condensed in a condenser 38 to a temperature of about 0. to 10 80°C. The condenser 38 typically uses water or air as a heat transfer means. The cooled base is then conducted through line 36 into the anode compartment 20 to replenish the base therein. The liquid acid component remaining in the thermal regenerator 12 after heating is conducted out through line 40, and optionally through cooler 42, and is 15 returned to the cathode compartment to replenish the acid therein. Solvent which was not volatilized by heating in the thermal regenerator 12 is carried along with the acid component.

20       The thermoelectrochemical system shown in FIG. 1 may be operated using a variety of acid-base systems. Examples of such systems include, but are not limited to, those listed below.

- 25       a. Pyridine - methylsulfonic acid
- b. Pyridine - hydrochloric acid
- c. Pyridine - phosphoric acid
- d. Pyridine - trifluoromethylsulfonic acid
- e. Acetic acid - triethanolamine
- f. Acetic acid - monoethanolamine
- g. Acetic acid - diethylamine
- 30       h. Acetic acid - pyridine
- i. Benzoic acid - ammonia
- j. Aniline - hydrochloric acid
- k. Ammonia - borate ester [condensation product of boric acid and ethylene glycol]
- 35       l. Lactic acid - diethylamine

1 An exemplary electrode apparatus in accordance with  
the present invention is shown generally at 50 in FIG. 2.  
The apparatus 50 includes a central membrane 52 which can  
be made from electronically non-conductive carbon felt  
5 which is available from Fiber Materials, Inc. (Biddeford,  
Maine). The carbon felt which functions as membrane 52 is  
a very fine mesh felt material. It is believed that gas  
passes through or along the carbon fibers, to provide gas  
permeable regions in membrane 52. The openings between  
10 the fibers of the carbon felt are filled with a cation  
exchange material such as Nafion, for example, by adding  
the felt to a 5% solution of Nafion and boiling the  
solution to dryness. The Nafion regions in the felt  
function as the ion permeable regions when the membrane is  
15 saturated with solution during use as electrode apparatus  
21 in an electrochemical cell such as 10 shown in FIG. 1.  
The composite carbon felt-Nafion membrane may be  
visualized as a Nafion membrane having carbon fibers  
extending from one edge of the membrane to the other.

20 Anode means are provided on a first side of  
membrane 52. The anode means includes a layer of porous  
electrode material 54 comprising a carbon-teflon mixture  
impregnated with approximately  $0.25 \text{ mg/cm}^2$  of platinum.  
Other porous hydrogen electrode materials can be utilized  
25 provided they have sufficient porosity to allow migration  
of gas and ions through the anode while providing desired  
hydrogen electrode characteristics. The porous layer 54  
can be prepared, for example, by separating the catalyst  
layer from the hydrophobic backing of a fuel cell  
30 electrode manufactured by Energy Research Company  
(Danbury, Connecticut). This separated catalyst layer is  
then pressed against the first side of membrane 52.  
Optionally, a porous electrode may be formed by depositing  
platinum black on a fine metal screen.

1        Current collector means for collecting current from  
the anode porous layer 54 are provided by, for example, a  
layer of electronically conductive graphite felt 56 and/or  
gold plated fifty mesh screen 58 formed of tantalum,  
5        stainless steel, or other non-corrosive metal. The  
graphite felt layer 56 may be type VDG which is available  
from Union Carbide Company, New York, New York. Cathode  
means are provided on the second side of membrane 52. The  
cathode means includes the same layers as the anode  
10      means. These layers include porous electrode material  
layer 60, conductive carbon felt layer 62 and current  
collector screen 64. The electrode apparatus shown in  
FIG. 2 was tested as described in Example 1 herein.

15      A second exemplary electrode apparatus in accordance  
with the present invention is shown generally at 70 in  
FIG. 3. The apparatus 70 is the same as apparatus 50 in  
FIG. 2 in that it includes a central gas- and ion-  
permeable membrane 72, porous anode layer 74, porous  
cathode layer 76 and current collectors 78 and 80. In  
20      this embodiment, the membrane 72 is constructed by placing  
small (1 mm) drops of five percent Nafion solution  
(obtained from Solution Technology Inc., Mendenhall,  
Pennsylvania) onto selected regions of a piece of  
hydrophobic microporous polypropylene (Celgard 2500, from  
25      Celanese Corp., Charlotte, North Carolina). The membrane  
is air dried and then cured at 120°C for ten minutes.  
The Nafion solution produces regions permeable to cations  
as represented schematically at 82, with the remaining  
gas-permeable, ion-impermeable regions of the hydrophobic  
30      microporous polypropylene being represented at 84. The  
porous electrode layers 74 and 76 can be made from the  
same material as in apparatus 50 of FIG. 2 and the current  
collectors 78 and 80 can be provided by graphite felt, for  
example. The electrode apparatus 70 was tested as  
35      described in Example 2 herein.

I        A third exemplary electrode apparatus in accordance with the present invention may be prepared by taking two pieces of porous (expanded) PTFE backed fuel cell electrodes from Energy Research Company and modifying these electrodes by coating the PTFE backing with five percent Nafion solution. The Nafion solution partially soaks into the PTFE to provide areas of ion permeability in the otherwise ion-impermeable PTFE layer. The two electrodes are pressed together with the two PTFE surfaces in contact. The assembly is cured at 120°C for one-half hour to bond the two pieces together. The resulting structure comprises a sandwich structure including, from the outside in: (a) the two electrodes; (b) adjacent regions of porous teflon containing islands of Nafion; and (c) a central region containing islands of Nafion. Alternatively, a Nafion-impregnated teflon composite may be simply pressed against fuel cell electrodes. The teflon is vacuum impregnated at 180°C with the Nafion by dissolving Nafion in dimethyl sulfoxide (DMSO) and drawing this solution into the teflon. The vacuum treatment is continued until all of the DMSO evaporates. After the composite has cooled, hot DMSO (110°C) is used to wipe excess Nafion from both surfaces of the membrane composite. Optionally, electrode means may be provided by vacuum impregnating a slurry of platinized activated carbon into the external pores (i.e. pores at or near the surface) of both sides of the membrane composite and bonding the electrodes to the membrane pores using Nafion solutions.

3.0      Collector means for each electrode are provided, for example, by tantalum screens which are embedded in the catalyst layers. A hydrogen manifold for introducing hydrogen gas into the membrane assembly is prepared by bonding a non-conductive tube to one edge of the assembly. RTV 3145 Sealant (from Dow Corning, Midland,

1 Michigan) can be used to seal the remaining three edges of the assembly. This assembly and an alternative thereof were tested as described in Examples 3 and 4 herein.

5 A fourth exemplary electrode apparatus in accordance with the present invention may be prepared using a commercially available porous ion-permeable membrane, such as porous Nafion, as the separation membrane and pressing commercially available fuel cell electrodes against the membrane. The gas passes through the pores in the  
10 membrane, while the ions pass through the membrane itself. This type of electrode apparatus was tested as described in Example 5.

#### EXAMPLE 1

15

This example illustrates the testing of the electrode apparatus shown in FIG. 2, using a composite carbon felt-Nafion membrane. The electrode apparatus was constructed as previously described herein. In the first  
20 test described below, methylsulfonic acid was used as the cell fluid on both sides of the membrane. The purpose of this initial test was to prove that both gas and ions can be efficiently transported across the membrane. In the second test described below, other system fluids were used  
25 to provide improved efficiency in the passage of ions (or current) and gas.

The electrode apparatus shown in FIG. 2 was tested by immersion in a mixture of three moles water to one mole methyl sulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ). A hypodermic needle  
30 was inserted into the membrane 52 to supply hydrogen thereto from a hydrogen gas cylinder. When current was applied to the assembly 50, hydrogen was produced at the cathode layer 60. This hydrogen is expected to diffuse through the membrane 52 and be consumed at the anode  
35 layer 54. Simultaneously, protons diffuse through

1 membrane 52 from the anode 54 to the cathode 60. 5  
Polarization measurements were taken with a Model 363  
potentiostat/ galvanostat (obtained from Princeton Applied  
Research Company, Princeton, New Jersey). Polarization  
5 tests are considered to be a good indication of the  
ability of an electrode apparatus to generate current when  
utilized in electrochemical cells of the type shown in  
FIG. 1. Since polarization represents the resistance or  
inefficiency of the system, a low polarization voltage is  
10 desirable. The results of the polarization tests  
conducted at room temperature were as follows:

	<u>Current Density (ma/cm<sup>2</sup>)</u>	<u>Polarization (mV)</u>
15	0.2	7
	2.0	74
	20.0	580

20 The results described above are interesting, but they  
do not prove that hydrogen from the cathode was passing to  
the anode, since hydrogen was fed to the electrode from an  
external source.

25 In a second test of the composite membrane electrode  
apparatus of FIG. 2, lactic acid (LA) and diethylamine  
(DEA) were used as the cell fluids. The test was  
conducted as described above except that the introduction  
of hydrogen through a hypodermic needle was omitted. The  
cathode compartment contained an acidic mixture consisting  
30 of 2.0:1.0:2.0 mole parts LA:DEA:H<sub>2</sub>O, and the anode  
compartment contained a basic mixture consisting of  
1.8:1.0:5.0 mole parts DEA:LA:H<sub>2</sub>O. The electrode  
apparatus was bathed in pure H<sub>2</sub> at 4.2 psig prior to  
filling the anode and cathode compartments with the above  
liquid mixtures. It is this initially placed hydrogen  
35 which is counted upon to be trapped along the carbon fiber

I passages when the cell is filled with liquid acid and base. Tests were started at 74°C. The open circuit voltage was 0.29 volts. The short-circuited current decreased from 1.5 ma/cm<sup>2</sup> to 0.2 ma/cm<sup>2</sup> after 5 60 minutes. At room temperature, currents of 0.2 ma/cm<sup>2</sup> could also be sustained.

It appears that these results were due to hydrogen dissolved in the cell fluids acting as a hydrogen source to the anode rather than due to the diffusion of hydrogen through the membrane from the cathode to the anode. In 10 addition, the lack of temperature dependence in the experiments on the composite carbon-Nafion membrane suggests that gas solubility and diffusion are rate-controlling. From these results, it appears that the 15 composite carbon-Nafion membrane was not capable of passing hydrogen gas at the fluxes required to provide an operable system.

For purposes of comparison, the carbon felt described above was tested without the addition of Nafion. It was 20 found that in a cell using this structure as the separation membrane, currents could be maintained only so long as external hydrogen was pumped in. Thus, this structure did not allow hydrogen gas to pass through the membrane.

25

#### EXAMPLE 2

This example illustrates the testing of the electrode apparatus shown in FIG. 3. The electrode apparatus was 30 constructed as previously described herein.

The electrode apparatus shown in FIG. 3 was tested for polarization in the same manner as described in Example 1. The results were as follows:

	<u>Current Density (ma/cm<sup>2</sup>)</u>	<u>Polarization (mV)</u>
	0.2	32
5	2.0	350
	4.0	670

I 10 The apparatus 70 operated stably at 2.0 ma/cm<sup>2</sup> with the hydrogen supply shut off. By contrast, the electrode assembly 50 shown in FIG. 2 could maintain currents only briefly once the hydrogen supply was stopped, as previously discussed.

#### EXAMPLE 3

I 15 This example illustrates the testing of the third exemplary electrode apparatus of the present invention, comprising Nafion-soaked PTFE layers bonded together. The electrode apparatus was constructed as generally described herein to provide the sandwich structure previously noted.

20 This electrode apparatus was tested for polarization in the same manner as described in Example 1. The results were as follows:

	<u>Current Density (ma/cm<sup>2</sup>)</u>	<u>Polarization (mV)</u>
25	0.2	5
	5.0	47
	50.0	377

30 This assembly operated stably for 20 minutes with the hydrogen supply shut off.

#### EXAMPLE 4

35 This example illustrates testing of an alternative to the third exemplary electrode apparatus of the present invention comprising a Nafion-impregnated teflon composite.

1        This electrode was constructed as follows. Expanded  
      teflon of 1.0 micrometer (0.0001 cm) nominal pore size was  
      treated with Nafion to make a Nafion-teflon composite  
      which contained about 35% Nafion and 65% teflon.

5        Permeability measurements showed that this composite  
      passed  $H_2$  gas at a rate of  $0.1 \text{ cm}^3/\text{sec. cm}^2 \text{ psi}$   
      where psi refers to a differential pressure of one pound  
      per square inch.

10      Electrodes were attached to the membrane composite as  
      follows. Activated carbon, sold as Black Pearls 2000 by  
      Cabot Company of Boston, Massachusetts, was platinized and  
      a slurry of the carbon was drawn into the external pores  
      of the membrane composite by vacuum impregnation. This  
      membrane composite had a thickness of approximately 15  
      mils (0.375 mm).

15      A  $2 \text{ cm}^2$  electrode membrane composite combination was  
      mounted in a glass cell and exposed to 1 atmosphere of  
      hydrogen at room temperature. The anode compartment was  
      then filled with a 15 weight percent ammonia, 85 weight  
      percent water solution. The cathode compartment was  
      filled with a solution made up from 0.80 mole fraction  
      boric acid and 0.20 mole fraction ethylene glycol. This  
      mixture forms an acid containing a borate-glycol ester  
      anion by a condensation process involving elimination of  
      20     water. The open circuit voltage of this cell was  
      0.225 volts. The short circuit current at room  
      temperature was  $2.0 \text{ ma/cm}^2$ . The current-voltage plot  
      25     was linear over the entire range.

30      In a separate test, electrodes were attached to the  
      membrane composite by pressing against the membrane, fuel  
      cell electrodes obtained from Prototech Company of Newton  
      Highlands, Massachusetts, and having  $0.5 \text{ mg/cm}^2$  platinum  
      loading. Using the same cell fluids as noted above, this  
      35     system provided about 10 percent lower current at short  
      circuit than the previous system using activated carbon.

I However, when a lactic acid-diethylamine fluid system was substituted for the borate-ammonia system, the short circuit current dropped to 0.55 ma/cm<sup>2</sup>.

5

EXAMPLE 5

This example illustrates the testing of the fourth exemplary electrode apparatus of the present invention comprising a porous Nafion separation membrane.

10 A 21-mil (0.525 mm) thick porous Nafion membrane was obtained from Solution Technology Inc. of Mendenhall, Pennsylvania. Fuel cell electrodes obtained from Prototech Company of Newton Highlands, Massachusetts and identical with those used in Example 4, were pressed  
15 against the membrane. The assembly was mounted in test equipment that circulated temperature-controlled acid and base fluids past the cathode and anode respectively. The equipment also fed hydrogen or nitrogen gas to the edge of the anode. The working fluids comprised acidic and basic  
20 mixtures of lactic acid and diethylamine. The acidic mixture was made up by adding 103 ml of diethylamine and 36 ml of water to 204 ml of 75% by weight aqueous solution of lactic acid. The basic mixture was made up by adding 189 ml of diethylamine and 90 ml of water to 103 ml of 75%  
25 lactic acid.

At 60°C, the initial resistance of the 2.0 cm<sup>2</sup> cell was 20 to 30 ohms, which was 3 to 5 times the value measured under comparable conditions with the thin Nafion-Teflon composite membrane used in Example 4. Early  
30 in the experiment, the short-circuit current was 9 mA. Over a period of 18 hours, the short-circuit current gradually decayed to 0.4 mA. At this stage, the current was the same whether nitrogen or hydrogen gas was fed to the edge of the anode. Coulombic data recorded during a  
35 3-hour run with the anode and cathode compartments and the

1      gas edge feed under a blanket of nitrogen showed  
unequivocally that hydrogen consumed by the anode must  
have travelled through the pores in the Nafion membrane.

5      This test demonstrates the viability of a cell based  
on porous Nafion as the separator material. The thickness  
of the available membrane, and the physical characteristics  
of the electrodes prevented achievement of optimum cell  
performance. Approaches for reaching optimum performance  
include fabrication of thinner porous Nafion membranes and  
10     the use of thinner electrodes, and better contact between  
the electrodes and the membranes. For example, an  
electrode apparatus could be formed as described in  
Example 4 by depositing catalyst particles within the  
surfaces of the membrane or as described earlier by  
15     thermal compression bonding and/or curing with Nafion  
solution used as a glue. By such bonding, thin catalyzed  
sheet electrodes can be bonded to the membrane or  
catalyzed particles within the external pore structure of  
the membrane can be bonded to the membrane structure. It  
20     is anticipated that with such optimization, cell  
performance comparable to those discussed in Examples 2-4  
can be obtained.

25     These results presented in Examples 2-5 indicate the  
effectiveness of the electrode apparatus of the present  
invention for providing for the transfer of both gas and  
ions in an operating electrochemical cell. It is  
recognized that the current obtained was lower than is  
desired for an operating system. However, significant  
improvements in current may readily be obtained by: (a)  
30     increasing the temperature in the electrochemical cell;  
(b) optimizing the contact and/or bonding between the  
membrane composite and the electrodes; (c) making the  
electrodes thinner, for example, within the range of 1 to  
4 mils (0.0025 to 0.01 cm); (d) making the separation  
35     membrane thinner; and/or (e) optimizing the electrode

1      composition and structure to accommodate liquid flow.  
- Thus, when used in such an optimized system it is  
    anticipated that the electrode apparatus of the present  
5      invention can provide current at the levels required for  
    practical application.

10     Although the present invention has been described in  
    detail with regard to exemplary embodiments involving  
    acid-base type thermoelectrochemical cells, it should be  
    understood that the invention is not limited to use only  
15     in these types of cells. Rather the present invention has  
    wide application to any type of electrochemical cells  
    where it is necessary to have combined transport of both  
    gas and ions between the electrodes for proper cell  
    operation. Those skilled in the art will recognize that  
15     the within disclosures are exemplary only and that various  
    other alternatives, adaptations and modifications may be  
    made within the scope of the present invention.  
    Accordingly, the present invention is not limited to the  
20     specific embodiments as illustrated herein, but is only  
    limited by the following claims.

CLAIMSWhat is Claimed is:

I 1. An electrode apparatus adapted for use in an electrochemical system having an anode compartment and a cathode compartment in which gas and ions are produced and consumed in said compartments during electrical current 5 generation by said system, wherein said electrode apparatus comprises:

I0 a membrane for separating said anode compartment from said cathode compartment, said membrane having a cathode side and an anode side and comprising ion-permeable regions to provide transfer of ions between the cathode and anode sides of the membrane and gas-permeable regions to provide transfer of gases between the cathode and anode sides of the membrane;

I5 cathode means located in the cathode compartment on said cathode side of the membrane and in contact with said membrane for generating electric current; and

20 anode means located in the anode compartment on said anode side of the membrane and in contact with said membrane for generating electric current wherein gas and ions generated at said cathode means and anode means migrate through said membrane to provide transfer of said gas and ions between said anode and cathode compartments.

1 2. An electrode apparatus according to claim 1 wherein said anode means and said cathode means comprise hydrogen electrodes and said gas comprises hydrogen.

1 3. An electrode apparatus according to claim 1 wherein said ion-permeable regions are provided by ion-permeable materials selected from the group consisting

5 of cation exchange materials or membranes, anion exchange materials or membranes and microporous hydrophilic membranes.

I 1 4. An electrode apparatus according to claim 1 wherein said gas-permeable regions are provided by a hydrophobic microporous membrane material.

I 2 5. An electrode apparatus according to claim 4 wherein said gas permeable material comprises hydrophobic microporous polypropylene or microporous polytetrafluoroethylene.

I 3 6. An electrode apparatus according to claim 1 wherein said membrane comprises an ion-permeable membrane having formed therein at selected locations gas-permeable regions.

I 4 7. An electrode apparatus according to claim 6 wherein said gas-permeable regions comprise openings in said ion-permeable membrane.

I 5 8. An electrode apparatus according to claim 1 wherein said membrane comprises a gas-permeable membrane having formed therein at selected locations ion-permeable regions.

I 6 9. An electrode apparatus according to claim 1 wherein said membrane comprises gas-conducting fibers in the form of a felt, said felt having ion-conducting material in the spaces between said fibers to allow 5 passage of ions therethrough.

I 7 10. An electrode apparatus according to claim 9 wherein said gas-conducting fibers are selected from the

group consisting of electronically non-conducting carbon, porous polytetrafluoroethylene, and porous polypropylene.

- 1 11. An electrode apparatus according to claim 1 wherein said membrane comprises a hydrophobic material in the form of a felt, mesh, paper, cloth or porous film having openings of relatively small and relatively large sizes to allow passage of gas through said openings of small size and passage of ions through said openings of large size.
- 1 12. An electrode apparatus according to claim 1 wherein said cathode means comprises a layer of porous electrode material on the cathode side of said membrane.
- 1 13. An electrode apparatus according to claim 1 wherein said anode means comprises a layer of porous electrode material on the anode side of said membrane.
- 1 14. An electrode apparatus according to claim 12 wherein said anode means comprises a layer of porous electrode material on the anode side of said membrane.
- 1 15. An electrode apparatus according to claim 12 wherein said cathode means includes current collector means in contact with said porous electrode material for collecting electrical current generated thereby.
- 1 16. An electrode apparatus according to claim 13 wherein said anode means includes current collector means in contact with said porous electrode material for collecting electrical current generated thereby.
- 1 17. An electrode apparatus according to claim 14 wherein said porous electrode material comprises a carbon-polytetrafluoroethylene mixture impregnated with platinum.

I 18. An electrode apparatus according to claim 14  
wherein said porous electrode material comprises  
polytetrafluoroethylene impregnated with platinum.

I 19. An electrode apparatus according to claim 15  
wherein said current collector means comprises:  
an electrically conductive screen; and  
a layer of electronically conductive felt located  
5 between and in contact with said conductive screen and  
said porous electrode material.

I 20. An electrode apparatus according to claim 16  
wherein said current collector means comprises:  
an electrically conductive screen; and  
a layer of electronically conductive graphite felt  
5 located between and in contact with said conductive screen  
and said porous electrode material.

I 21. An electrode apparatus according to claim 1  
wherein:  
a) said membrane comprises electronically  
non-conductive carbon felt impregnated with a polymer of  
5 polytetrafluoroethylene with fluorinated ether side chains  
terminated with sulfonic acid groups; and  
b) said anode means and said cathode means each  
comprise:  
10 1) an electrode comprising a carbon-polytetra-  
fluoroethylene mixture impregnated with platinum;  
2) a layer of electronically conductive graphite  
felt contacting said electrode; and  
3) a layer of gold plated mesh screen contacting  
said electronically conductive graphite felt.

I 22. An electrode apparatus according to claim 1  
wherein:

5 a) said membrane comprises hydrophobic microporous polypropylene including at selected locations regions of a polymer of polytetrafluoroethylene with fluorinated ether side chains terminated with sulfonic acid groups; and

b) said anode means and said cathode means each comprise:

10 1) an electrode comprising a carbon-polytetrafluoroethylene mixture impregnated with platinum; and  
2) a layer of electronically conductive graphite felt contacting said electrode.

1 23. An electrode apparatus according to claim 1 wherein:

5 a) said membrane is formed from two layers of porous polytetrafluoroethylene each coated on a first side with a polymer of polytetrafluoroethylene with fluorinated ether side chains terminated with sulfonic acid groups, and bonded together on a second side opposite said first side;

b. said anode means and said cathode means each comprise:

10 1) an electrode comprising a carbon-polytetrafluoroethylene mixture impregnated with platinum; and  
2) a layer of electronically conductive graphite felt contacting said electrode.

1 24. An electrode apparatus according to claim 1 wherein said membrane is bonded to said anode means and said cathode means.

1 25. An electrode apparatus according to claim 1 wherein said membrane comprises porous polytetrafluoroethylene impregnated with a polymer of polytetrafluoroethylene with fluorinated ether side chains terminated 5 with sulfonic acid groups.

1        26. An electrode apparatus according to claim 25  
wherein said anode means and said cathode means comprise a  
material selected from the group consisting of platinized  
activated carbon particles, platinum-impregnated teflon,  
5        and platinum particles, located within and bonded to the  
external pores of said membrane.

1        27. An electrode apparatus according to claim 1  
wherein said electrochemical system comprises lactic acid  
and diethylamine.

1        28. An electrode apparatus according to claim 1  
wherein said electrochemical system comprises ammonia and  
borate ester.

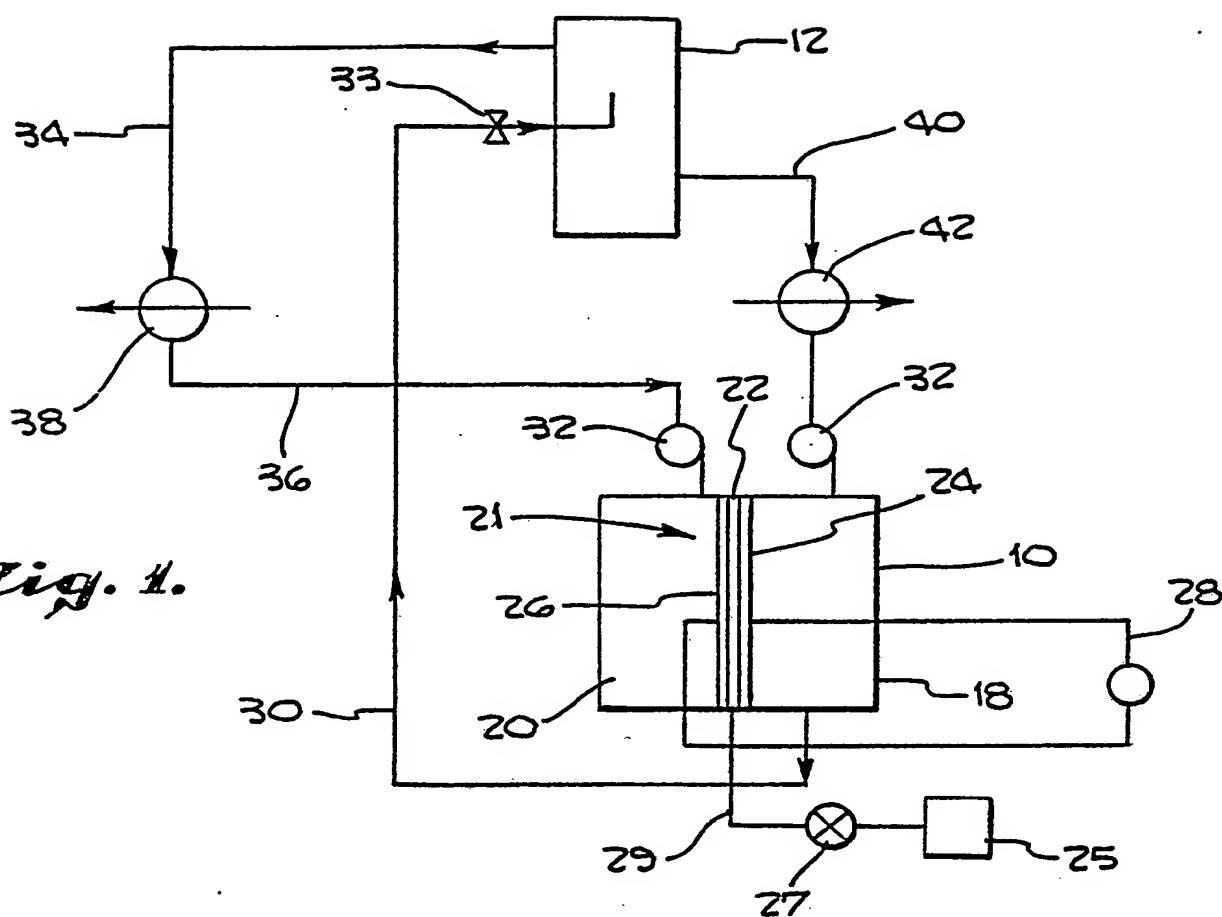


Fig. 1.

Fig. 2.

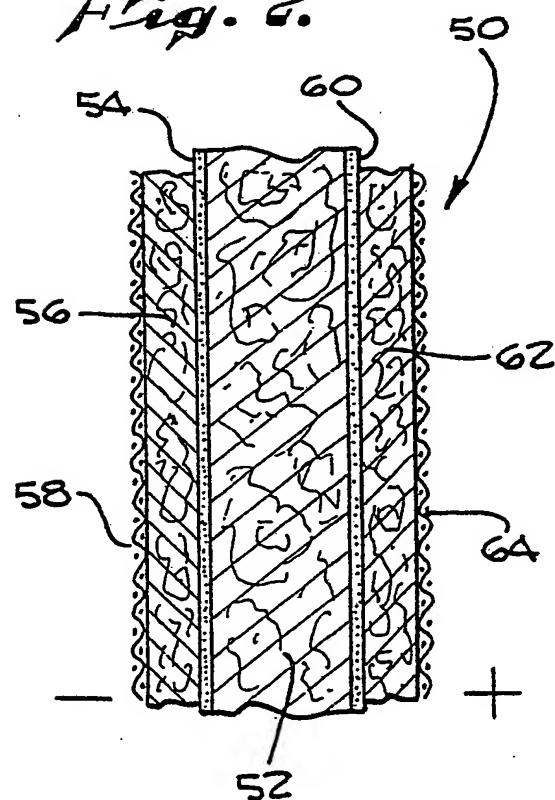
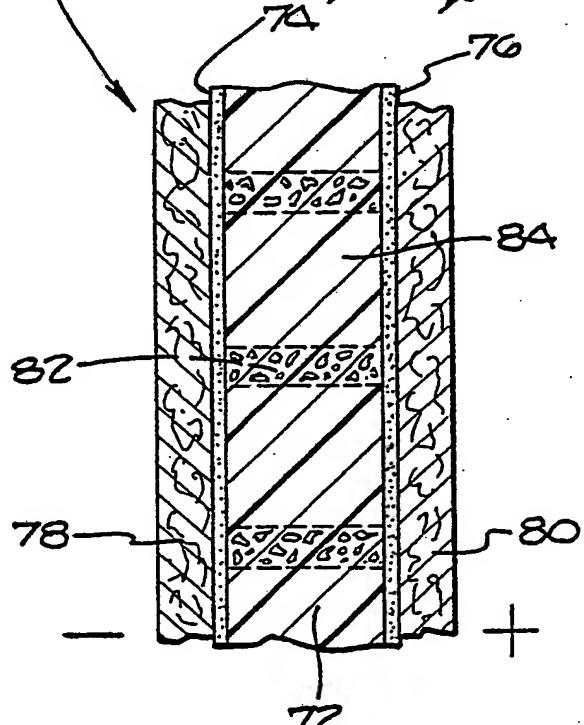


Fig. 3.



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 88/02062

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>4</sup>: H 01 M 8/18; // H 01 M 2/14

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
IPC <sup>4</sup>	H 01 M
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT\*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	US, A, 3231426 (F.A. LUDWIG) 25 January 1966 see figure 1; column 2, line 53-60; column 3, line 3-47; column 5, line 20-37, 49-55; claim 1 ---	1,6,7
A	DE, A, 3302635 (BECKER FRIEDRICH) 2 August 1984 see figure 1; claim 1, page 3 last paragraph; page 4, lines 17-22 ---	1,2,8
A	DE, A, 3239992 (BECKER FRIEDRICH) 3 May 1984 see claims 1,8,12; page 3 last paragraph; page 4, paragraph 3; page 6, lines 4-11 ---	1,8,9,10
A	US, A, 3764387 (R.E. STACK) 9 October 1973 see figure 3, column 3, lines 44-58, column 4, lines 17-33 ---	
A	GB, A, 1020171 (UNION CARBIDE) 16 February 1966 see claims 1,8,9 ---	

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"G" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

10th October 1988

Date of Mailing of this International Search Report

2 NOV 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

P.C.G. VAN DER PUTTEN

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	GB, A, 791075 (H. VOGT) 26 February 1958 see pages 2, lines 26-27, lines 84-131 ---	
A	US, A, 3438812 (S. CHERNEY et al.) 15 April 1969 see column 5, lines 13-20; column 5, line 75 - column 6, line 4 ---	
A	GB, A, 2039133 (GENERAL ELECTRIC COMP.) 30 July 1980 ---	
P,A	US, A, 4738904 (F.A. LUDWIG et al.) 19 April 1988 -----	

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ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 8802062  
SA 23280

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 25/10/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 3231426		None		
DE-A- 3302635	02-08-84	DE-A-	3239992	03-05-84
DE-A- 3239992	03-05-84	DE-A-	3302635	02-08-84
US-A- 3764387	09-10-73	None		
GB-A- 1020171		None		
GB-A- 791075		US-A-	2991324	
		DE-A-	1042681	
US-A- 3438812	15-04-69	None		
GB-A- 2039133	30-07-80	US-A-	4215183	29-07-80
		FR-A,B	2446015	01-08-80
		DE-A,C	2951965	17-07-80
		JP-A-	55113272	01-09-80
US-A- 4738904	19-04-88	WO-A-	8802931	21-04-88
		AU-A-	8336887	06-05-88
		EP-A-	0286673	19-10-88